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MATERIAL SURFACE MODIFICATION FOR FIRST WALL PROTECTION*

MARK J. DAVIS

Sandia Laboratories, Albuquerque, New Mexico, 87185, USA**

The elements and strategy of a program to develop low Z surfaces for tokamak reactors is described. The development of low Z coated limiters is selected as an interim goal. Candidate materials were selected from the elements: Be, B, Al, Ti, V, C, O, N and their compounds. The effect of low energy erosion on surface morphology is shown for Be, TiC and VBe12. The trade-offs in coating design are described. Stress analysis results for TiB₂ coated POCO graphite limiters for ORNL's ISX-B tokamak are given.

KEY WORDS: Low Z Coatings / First Wall / Limiters / Physical Erosion

1. INTRODUCTION

The performance of materials facing the plasma in tokamaks is becoming a greater concern as plasmas get denser, hotter and burn longer. The material performance questions involve both material survival and plasma impurity generation. Research on surface modification is being conducted because it offers the designer flexibility. He can select optional surface materials to reduce plasma impurity levels at low cost since conventional first wall construction materials and techniques can be retained.

The use of surface modifying treatments such as discharge cleaning and Ti deposition to improve tokamak operations has been successful up to now. However, the reasons for the improvement are not always clear and unambiguous. It is for this reason that a large part of the current surface research effort in the DOE's fusion program is aimed at understanding the surface processes responsible for improved tokamak performance after surface modification.

The development of new surface modifications for the first walls of reactors is limited at this time by the lack of specific design requirements plus the lack of any devices operating with the appropriate burn time, plasma temperature and wall loading conditions to produce the erosion one expects in an EPR tokamak [1].

The first walls of current operating devices show no general erosion and in fact act as sinks for impurities generally produced from the limiter [2,3]. Hydrogen and impurity ions (i.e. oxygen, limiter materials and carbon) recycled and desorbed from the first wall are currently a serious problem in plasma operation.

These phenomena, however, fall outside the area of major concern for impurity generation in long burn EPR types of tokamak plasmas.

There are, however, two components facing the plasma in present tokamaks where erosion is of concern. They are limiters and wall armor or protective plates. These components can and will serve as test beds for evaluating low Z, erosion resistant surface modifications as near-term targets for coatings development. It is assumed that the successful development of low Z coatings for limiters today will establish design and evaluation techniques that will be used to develop first wall coatings in the years ahead.

2. COATING DEVELOPMENT PLAN

The specific surface modifications under development are low Z coatings for EPR first walls. The long-range development plan and strategy is presented in detail in [1]. Briefly, it consists of: 1) selecting the most important EPR coating properties, 2) developing screening tests to rank materials in terms of these properties, 3) screening materials, coatings and processes in the lab, 4) verifying the importance of the properties selected and measuring coating performance in a tokamak, 5) establishing materials, process and design standards for the better coatings, substrates and processes.

Since an EPR tokamak is a few years off, an intermediate goal has been selected. The goal is the development of low Z coated limiters for present and TFTR type tokamaks. In addition to the reasons given in the introduction, the achievement of this goal will have an impact on the plasma confinement program in the near term.

The first development will be a coated limiter for ISX-B during 1979. This development was started only after the following essential prerequisites were met: 1) a set of laboratory

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screening tests were established [4,5], 2) arrangements for tokamak testing in a hot, neutral beam heated plasma were made, and 3) the tokamak had plasma and in situ surface diagnostics to determine the effectiveness of the coatings in reducing impurities.

The strategy in this plan is to develop a broad, preliminary data base from screening tests and process studies to allow reasonable materials to be selected for development into coatings. In this way, materials with high physical erosion rates, or poor stability in hydrogen plasmas, etc, could be dropped early, and efforts to develop adherent coatings concentrated on a limited set of promising materials. The plan would also develop design practices so rational trade-offs can be made between coatings and processes for use in a specific tokamak.

2.1 Materials selection

Materials for low Z coatings are selected to have at least the following properties:

1) chemical stability in hydrogen plasma and during discharge cleaning, 2) low physical and physicochemical erosion rates, 3) low vapor pressure at operating temperatures, 4) low hydrogen and helium retention, and 5) radiation damage resistance. A more complete discussion is given in [1] and [6].

These requirements lead one to select materials from the elements Be, B, C, Al, Ti, V and their compounds. A list of coating-substrate materials under study in this coating program is given in Table 1.

Table 1
CANDIDATE COATING/SUBSTRATE COMBINATIONS

CHEMICAL VAPOR DEPOSITION	PLASMA SPRAY
TiB ₂ on C, Cu, 304SS, Ni, V, Ti, Mo, Ta	Be on Cu, 304SS, Mo, Ta, C, V
TiC on C, Cu, Mo, Ta	TiB ₂ on Cu, 304SS, Mo, Ta, C, V
B ₄ C on C, Mo, Ta, V	TiC on Cu, 304SS, Mo, Ta, C, V
SiC on C	W ₂ B ₁₀ on Cu, 304SS, Mo, Ta, C, V
B on C, 304SS	Al ₂ O ₃ on Cu, 304SS
BN on C	<u>SURFACE ENRICHMENT</u>
TiN on C	Be in Cu; Be in Ni; Be in Stainless Steel
<u>NITRIDING/CARBURIZING GAS PHASE</u>	Al in Cu; Al in Stainless Steel
Fe nitride, C, Ta nitride, V	Ti in Stainless Steel
	B in Stainless Steel

The threats to materials and the desired performance change considerably as one looks to the future. These changes are considered in our material selections. Today's first walls are cold, don't erode and aren't subject to much

radiation, while future first walls will be hot, sputtered and irradiated. Limiters are not as likely to change very much since they are now being designed to the thermal limits of materials. Wall armor will be expected to survive increased operating temperatures in the future. Its maximum thermal load under fault conditions will not change, however, since its upper limit is vaporization of the material. With improvements in neutral beam controls, wall armor may, in the future, operate at temperatures between the first wall and limiter conditions. Neutral beam shine through makes wall armor a possible candidate for blistering.

Absolute operating conditions in tokamaks are still vague but coating performance in tokamaks can be evaluated relative to known materials, i.e. stainless steel, carbon and molybdenum.

A particularly unsettling situation exists in materials selection because the relative importance of unipolar arcing, as a general source of impurities, in devices coming into operation is not clear. Their role in impurity generation in the past has been significant [7,8]. Though a number of studies are underway to evaluate, in the laboratory, unipolar arc resistance of materials and coatings, the only valid assessment will be based on tokamak performance. Particular attention is being placed on unipolar arcing in the design of coated limiter experiments to be conducted in ISX-B during 1979.

2.2 Coating process selection

Three types of processes are being characterized:

Additive, i.e. Chemical Vapor Deposition (CVD), Plasma Spraying, Cladding, Cementation

Reactive, i.e. Carburizing, Boriding, Nitriding

Autogenous, i.e. Surface segregation of low Z alloy constituents

The selection of a process to coat, for example TiC, depends as much on the application as it does on the quality of the coating produced. Chemical vapor deposition is a reasonable candidate for coating a 10 cm diameter, hemispherical limiter. It's not a particularly attractive candidate for coating 30 m² of wall armor for TFTR. Plasma spraying or pack cementation would be more economical candidates. In large area applications of coatings, the materials may be selected first on the basis of compatibility with a low cost process, and second on performance.

The possibility of developing a process into an in situ coating process is a very strong factor in its selection for further study. The importance will be in the future coating of reactor first walls and has been discussed previously [9,10]. The interest in CVD coating of TiC, TiB₂ and B₄C and reactive plasma nitriding,

boriding and carburizing is stimulated in part by the possibility of their development into in situ processes.

A compelling reason, other than cost, to develop more than one coating process for a material comes from the fact that different processes can create quite different coating morphologies.

This control can be an advantage since present devices would benefit from coatings with low surface area, because of less gas desorption. KPR tokamaks, however, should benefit from the more open structure found in plasma sprayed deposits because helium and hydrogen release should be enhanced [11,12].

Hot isostatic pressing (HIP) is a process which subjects materials to a "pressure cooker" type of treatment. Pressure of 200 MPa, and temperature to 2500K are used commercially. The HIP treatment is used to densify materials and heal internal cracks. It is being evaluated in this program as a means of improving the adhesion of coatings and to control coating density.

Plasma sprayed

density 82%

TiC

Plasma sprayed plus HIP

Be

100μ

The changes in microstructure produced by HIP of plasma sprayed TiC and Be are shown in Fig. 1. Both materials were HIPed at the same conditions. The TiC was unaffected itself by the HIP conditions (200 MPa hydrostatic pressure, 920K temperature and 4 hours time). The interface was densified because the copper substrate infiltrated the pores of the rigid plasma sprayed TiC. The beryllium was fully densified.

Erosion and adhesion testing of these materials is underway. It is hoped that the HIP treatment improves thermal fatigue strength of coatings as well as it has bulk materials.

In addition to the additive and reactive coating processes under study, autogenous surface enrichment is also being evaluated. In this work, stainless steel and nickel base alloys containing about 2 weight percent Al, Ti, Be and B are being evaluated with regard to any tendency to segregate their low Z constituents to the surface and retain them during erosion in a tokamak. Results by G. Nelson indicate that in Be-Hf, these processes only operate effectively at high temperatures (>1000K) where diffusion rates are high. This

Fig. 1. Effect of hot isostatic pressing* on plasma sprayed TiC (a) Be (b) * (200 MPa, 973K, 4 hrs).

suggests the limiter may be the most likely application now. Beryllium's high vapor pressure limits very high temperature use unless enough oxygen is present to form BeO on the surface. The rate of surface enrichment depends strongly on the presence in the atmosphere of elements that combine strongly with the Al, Ti, Be or B, such as oxygen, nitrogen or carbon. Some of Nelson's initial results are shown in Fig. 2. In this case, Be enriched itself on the surface at 723K, but during sputtering it could not replenish itself. This approach will require a detailed understanding of bulk and surface transport mechanisms and how they are affected by chemical reaction, radiation and physical erosion. The stainless steel alloys containing Al or Ti were developed by Bradshaw, et al [13]. The nickel beryllium and boron stainless are commercial alloys 440 and E300 40-B, respectively.

Fig. 2. Beryllium enrichment on Be-Ni alloy.

2.3 Coating Evaluation Plan and Results

The screening tests, discussed earlier, are being used to evaluate materials and coatings. They have been used singly and are: 1) chemical erosion, 2) physical erosion, 3) sputtering, 4) mechanical adhesion, and 5) thermal fatigue. A full report of recent results can be found in these proceedings [5].

The test philosophy stresses sequential tests with increasing accuracy and cost as materials pass the less expensive tests. For example, sputtering yields are only measured on coatings that have low erosion yields in the Kaufman ion etcher [4]. Tokamak testing will only be conducted on coatings that do well in the combined environment test discussed later.

Evaluation of the same material coated by different techniques is being conducted by A. Millendore to determine, in part, the role of coating density on the properties of interest.

Attention has been directed first at establishing steady-state surface morphologies prior to evaluating other properties, such as erosion rates. This concern is justified when one looks at the erosion rate of Be as a function of 1000 eV hydrogen ion dose (Fig. 3) [14].

Fig. 3. Erosion yield of Be as a function of dose.

The detailed morphology changes are shown in Fig. 4. In additional work on beryllium, D. Sharp and J. Panitz found the same conical morphology to develop after low energy hydrogen erosion, regardless of material processing, i.e. the eroded surface of single crystal beryllium appears the same as polycrystalline material as shown in Fig. 4.

This change in morphology with ion dose suggests that measurements of surface behavior be undertaken only on materials that have steady-state surface morphologies similar to those expected in service. One would expect, at a minimum, the gas desorption behavior to vary widely as the surface area increases.

Two examples of the initial microstructures and surface morphologies are compared with the surface morphology produced after low energy hydrogen ion erosion. Plasma sprayed and plasma sprayed plus HfPb TiC is shown in Fig. 5. Plasma sprayed and plasma sprayed plus HfPb VBe₁₂ is shown in Fig. 6. Plasma sprayed and plasma sprayed plus HfPb Be is shown in Fig. 7.

The erosion had little effect on the plasma sprayed TiC or VBe₁₂ other than to clean the surface. The fine cone structure was produced on the Be, as shown in Fig. 4.

Some materials have also been evaluated for hydrogen retention and remission in surface research programs. Preliminary research results on coated TiB₂ by K. Wilson, Fig. 8 [15], and B. L. Doyle, et al [16], suggest that the hydrogen recycle behavior of CVD TiB₂ is acceptable. Hydrogen is released upon heating above 600K, which is compatible with tokamaks such as TFTR whose limiters operate above 600K.

Evaporated Be before erosion

Single crystal Be before erosion

Eroded single crystal Be

Eroded single crystal Be

Evaporated Be after erosion

Single crystal Be after erosion

Fig. 4. Eroded surface morphology of evaporated and single crystal beryllium.

density 75%

plasma sprayed TiC

Plasma sprayed plus HIPed TiC

Plasma sprayed TiC, eroded by 7.4×10^{21} hydrogen ions. Flux $\approx 10^{16}$ ions/cm² sec at 250 eV.

5X view of the eroded surface at the left.

Fig. 5. Plasma sprayed TiC responses to HIP treatment and erosion

a Plasma sprayed VBe₁₂ density $\times 10^4$

b Cross section of plasma sprayed VBe₁₂

c Plasma sprayed VBe₁₂, eroded by 5.9×10^{21} hydrogen ions. Flux $\sim 10^{16}$ ions/cm² sec at 250 eV. Erosion yield .004.

d 5X view of 7c. (Note: the planar response compared with the conical response of Be in Fig. 5.)

Fig. 6. Plasma sprayed VBe₁₂ microstructure and erosion response to 250 eV hydrogen ions

Plasma sprayed Be

Plasma sprayed Be eroded by 5.9×10^{22} hydrogen ions. Flux $\approx 10^{16}$ ions/cm² sec at 250 eV

Fig. 7. Gross changes of plasma sprayed Be surface after low energy hydrogen ion erosion

Note: The cones shown in Fig. 5 require a larger magnification to resolve. At the magnification in Fig. 7b, the cones make the surface look like felt.

Fig. 8. Linear ramp desorption spectrum of CVD TiB₂ one hour after a fluence of 5×10^{18} ions/cm² of 10 keV D₃⁺ ions. Heating rate was 0.8 k/sec.

The next level of laboratory test will involve combined environments. The test apparatus and conditions are presented in Fig. 9. The combined environment tests are particularly important for evaluating stress-corrosion and corrosion fatigue behavior of coatings. This test will also serve as a final qualification for coating before tokamak test. The results of combined environment tests will show whether or not intermediate coating layers are necessary to stop cracks as well as provide better adhesion. The test will also reveal synergistic effects.

COMBINED ENVIRONMENT TEST CHAMBER

ENVIRONMENTS AVAILABLE

- Electron Beam - (A)
 - Pulsed or Continuous Heating
 - 0.1 sec, 15-20 kV
 - X-Y Scanning $\pm 45^\circ$, 500 Hz
 - 100 msec dwell time
 - 0.8-200 cm² Area
- Ion Beam - (B)
 - 200-2500 eV
 - 20 cm²
 - 0.5 mA/cm²
- Plasma - (C)
 - Sample Size: 0-1 kV
 - 0.5 mA/cm²

- #### DIAGNOSTICS:
- Optical Pyrometry
 - 18 Camera
 - 500 kcps
 - 16-channel Thermocouples
 - Deflection Gage
 - Residual Gas Analyzer
 - Optical Spectroscopy
 - Laser Spectroscopy

MATERIAL RESPONSES EXPECTED:

- Thermal Stress - Activation
- Ion Erosion - Physical
- Chemical
- Corrosion
- Applied Stress Response
- Thermal Desorption

Combined Effects

Fig. 9. Combined environment test chamber, 61 cm diameter and 97 cm long.

Synergistic effects between the thermal and mechanical loads are potentially severe for coatings. When one adds erosion and irradiation by 3.5 MeV alpha particles to the problem, it's quite formidable. The reader is referred to Section 3, C.6, in Reference 6 for further discussion.

2.4 Coating Design Approach

In the final analysis, coating performance will be determined in tokamaks. For this type of test to be meaningful, the coating-substrate and intermediate layers, if any, must be designed as a system to optimize thickness to best counter the erosive threat plus the mechanical and thermal stresses. An example of the results of a stress analysis for a coated ISX-B limiter is given in Fig. 10. The optimal coating thickness will vary depending on the method of coating, pulse intensity, repetition rate, and required life. In this case, the threat is essentially thermal.

Fig. 10. Thermo-mechanical stress analysis of a graphite limiter coated with 35 μ TiB_2 subjected to a heat flux of 2 kw/cm^2 for 0.2 sec.

Data in [5] indicate that the physical erosion rate of TiB_2 under a flux of 10^{16} ions/ cm^2 sec at 250 eV is about 10^{-11} cm/sec. If ten thousand 1-second shots were made in a year, only 0.1μ of coating material would be removed by low energy hydrogen ion erosion. In this situation, the coating thickness, 35 μ , was selected on the basis of process convenience, acceptable stress levels, an allowance for unipolar arc erosion and a front surface temperature low enough to keep the vapor pressure below 10^{-8} torr (610K in this case). An excess of coating material is also desirable, if it does not increase thermal stress too much, because of the threats unaccounted for above. Impurity ion sputtering or runaway electrons could have a large effect if the plasma is contaminated.

In this design, POCO graphite is used as a substrate because of its good adhesion with TiB_2 and TiC and adequate thermal shock resistance. Grade ASF-5Q was used since it gave the best balance of properties.

As tokamaks improve, coating designers will have to consider additional threats such as blistering. The work of Bauer, et al [17] suggests that too low a sputtering rate may invite blistering from 3.5 MeV alpha particles. The model presented in this work gives a quantitative way of determining blistering probability given accurate erosion data. Helium blistering won't be a very likely problem in the near future but is a concern in ETR. During neutral beam fault conditions, the incident deuterium flux on wall armor can be very high and of constant energy. These factors favor hydrogen blister formations, so one would try to design these plates to operate at temperatures high enough for redistribution of the hydrogen isotopes to reduce this type of blister formation but low enough to avoid excessive evaporation.

3. CONCLUSIONS

Low Z coatings have been applied to conventional materials and have been developed by surface segregation from certain low Z element containing alloys as a part of a long-range coating development plan.

The deposited coatings are generally adherent. Physical erosion rates in current tokamaks are low enough not to present a problem to TiB_2 , TiC or VBe_{12} coating 1 μ or more in thickness. Thermal fatigue, impurity ion erosion, unipolar arc erosion and possibly unidentified synergistic effects are the most threatening phenomena now and will be joined by low energy hydrogen ion erosion in the future.

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